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For presentation at the 243rd ACS National Meeting, San Diego, CA, 25-29 March 2012 and publication in Polymer Preprints, March 25, 2012.

14. ABSTRACT

Many hydrophobic surfaces exist in nature, but there is no naturally occurring oleophobic surface. There is plenty of academic and commercial interest in the development of oleophobic surfaces. The focus is on commercially available textiles. This presentation shows that fluoroPOSS are superhydrophobic. FluoroPOSS polymer composite surfaces can be superhydrophobic and superoleophobic. Superhydrophilic and superoleophobic surfaces have been developed. Such sufaces are ideal for the separation of both free-oil and oil-water emulsions. These membranes, for the first time, allow continuous-flow oil-water emulsion separation. Functionality will allow the covalent attachment of these low energy materials to substrates of choice.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Dr. Joseph M. Mabry
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THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER

Silicon-Containing Polymers and Composites

Silicones and Silicone-Modified Materials
ACS National Meeting
28 March 2012

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Motivation

- **Many hydrophobic surfaces exist in nature but there is no naturally occurring oleophobic surface**
- **Plenty of academic and commercial interest in the development of oleophobic surfaces**
- **Focus on commercially available textiles**

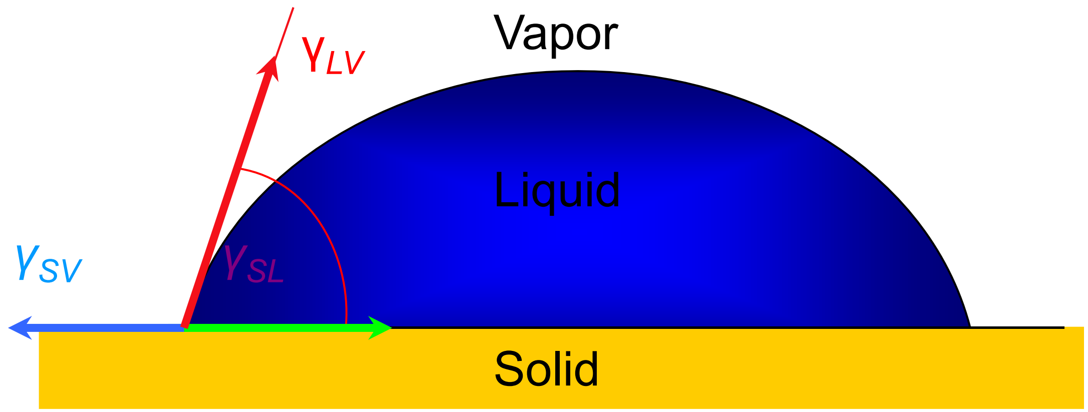
www.thedailygreen.com

www.gfn.com/sowhatsyourpoint/wp-content

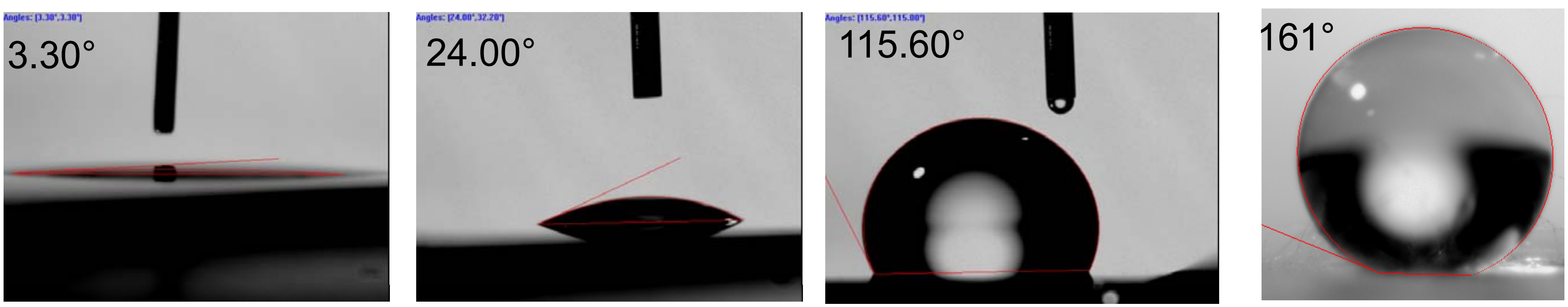
www. defense-technologynews.blogspot.com

www.tressugar.com

Non-wetting surfaces



Contact angles with water:

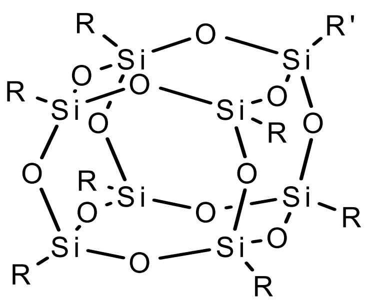


Superhydrophilic	Hydrophilic	Hydrophobic	Superhydrophobic
$\theta \sim 0°$	$0° < \theta < 90°$	$\theta > 90°$	$\theta^* > 150°$

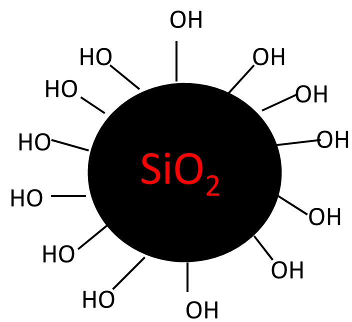
Similarly, superoleophobic surfaces display contact angle $\theta^* > 150°$ with oils or alkanes

Nanocomposite Materials

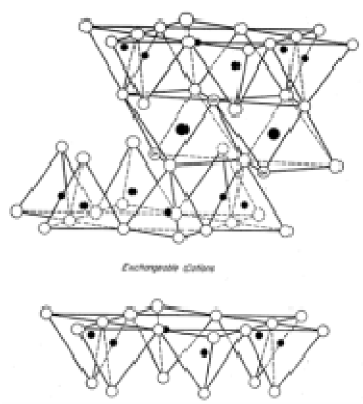
Silicon-containing compounds



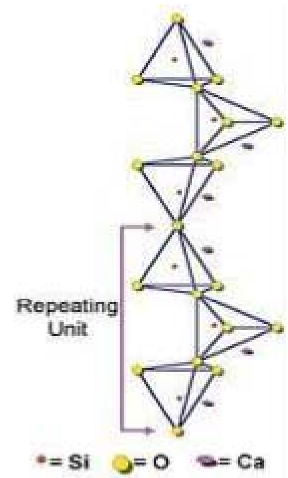
POSS



Nanosilicas



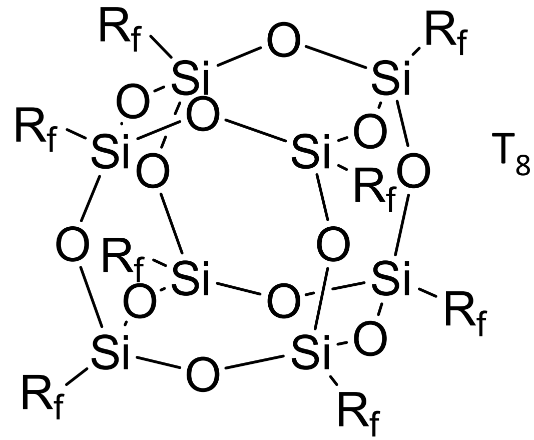
Layered silicates



Linear silicates

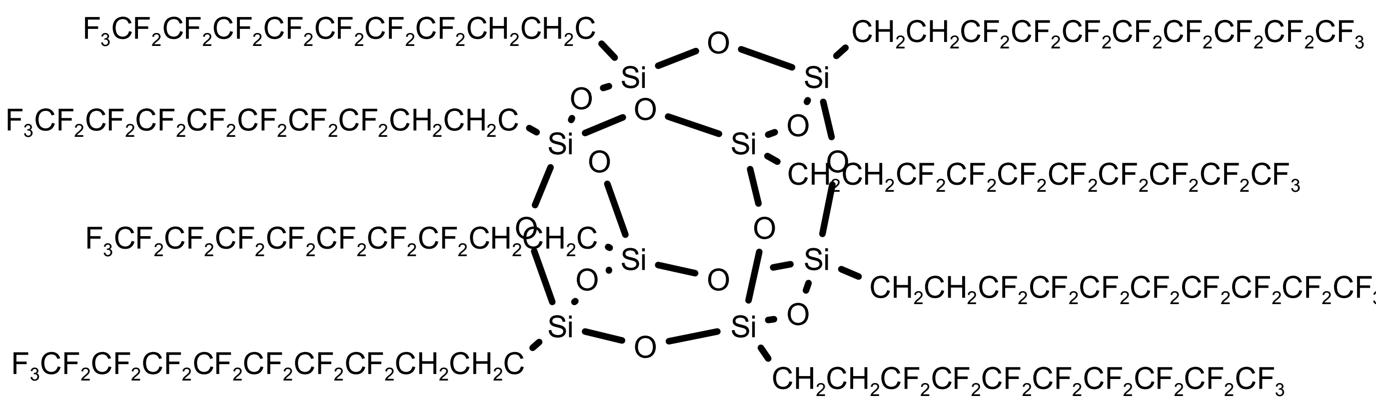
Fluorinated POSS Synthesis

$$R_fSiX_3 \xrightarrow[\text{solvent}]{OH^-/H_2O}$$



$R_f = -CH_2CH_2(CF_2)_nCF_3$

$n = 0, 3, 5, 7$



Angew Chem (2008)

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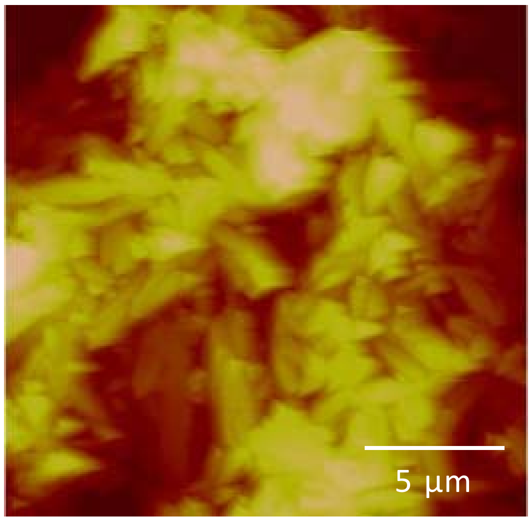
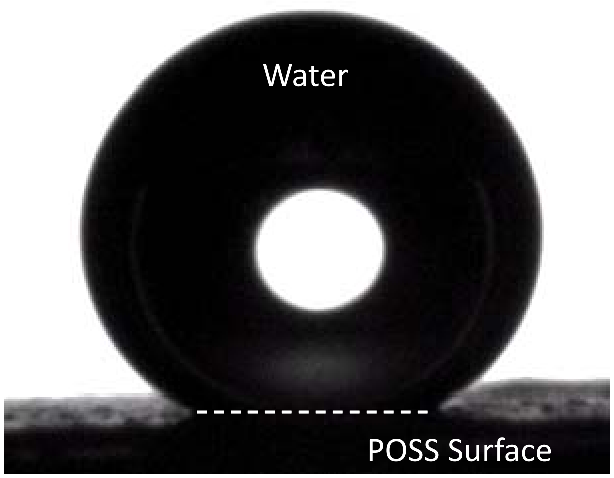
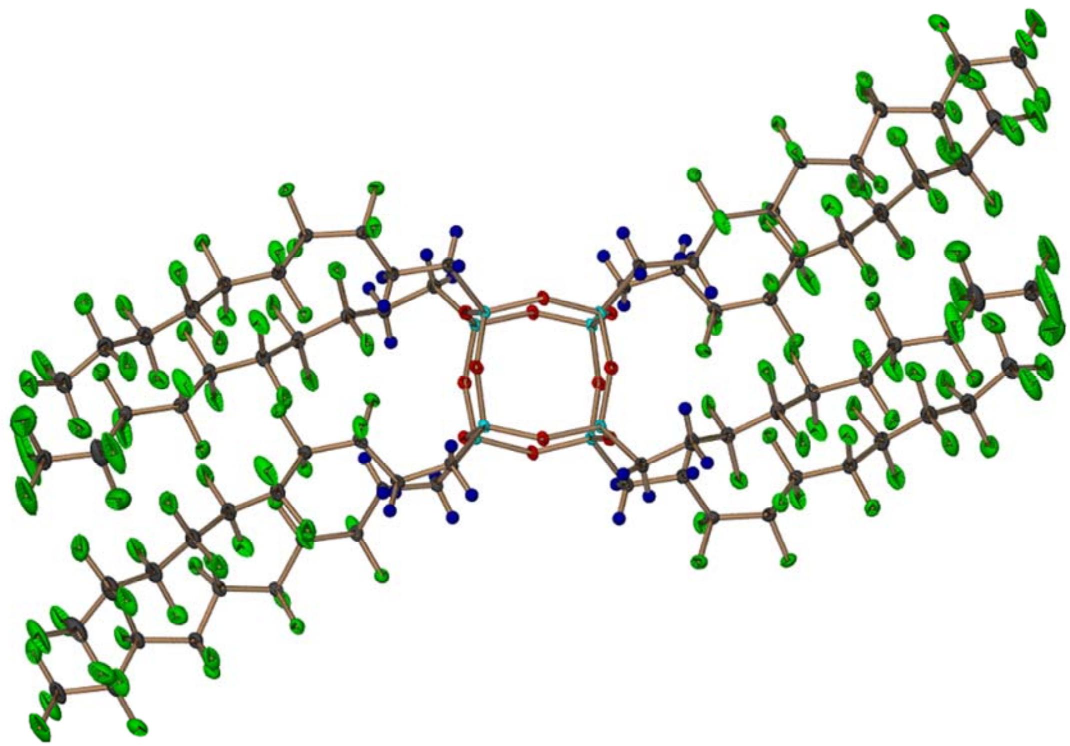
Hydrophobic Materials



- Spin-cast surface of Fluorodecyl POSS
- ~4 µm rms roughness by AFM
- 154° Water contact angle

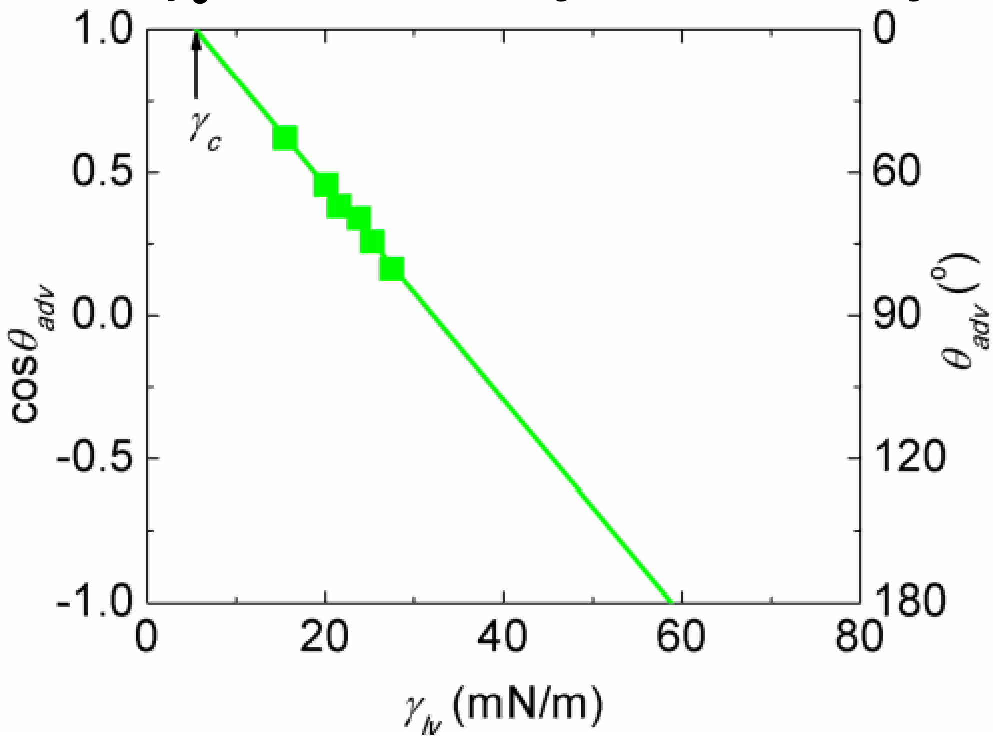


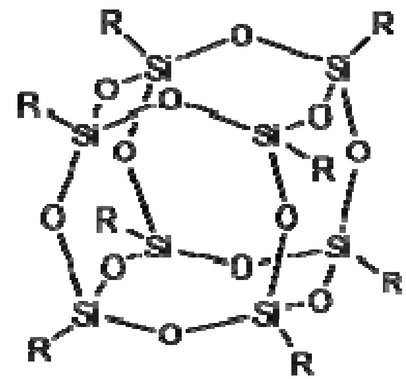


Angew Chem (2008)

Low Surface Energy Materials

γ_c = 5.5 mN/m by Zisman analysis





Fluorodecyl:
R = $-CH_2CH_2(CF_2)_7CF_3$

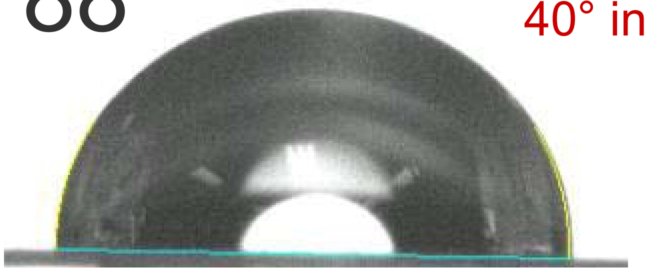
Similarly, GG analysis results in surface energy calculation of: γ_c = 8 mN/m

Contacting liquids:
hexadecane (γ_{lv} = 27.5 mN/m), dodecane (25.3), decane (23.8), octane (21.6), heptane (20.1), and pentane (15.5)

ACS AMI (2010)

Water/Oil Repellant Nanocomposites

88°

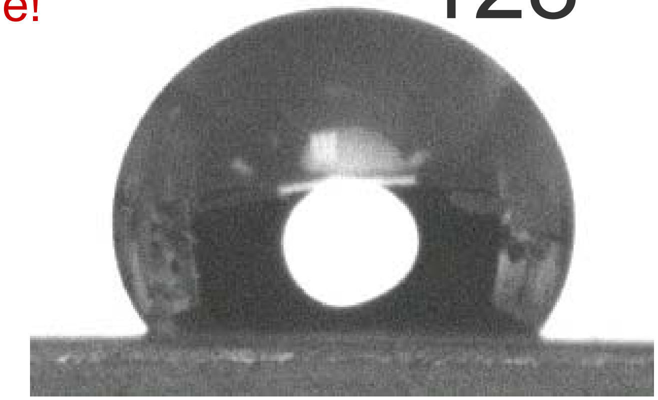


Polychlorotrifluoroethylene (PCTFE)

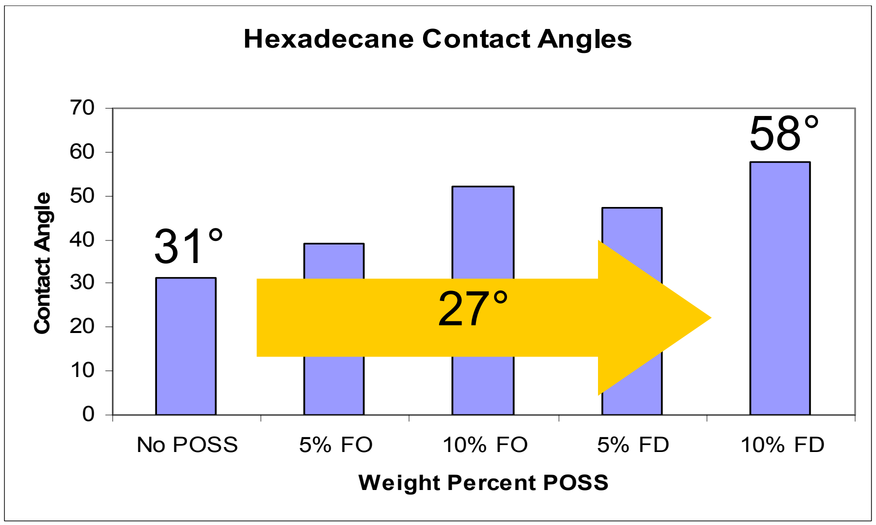
40° increase in water contact angle!

10% POSS

128°



PCTFE with 10% Fluorodecyl$_8$T$_8$



Increase in hexadecane contact angle less than desired

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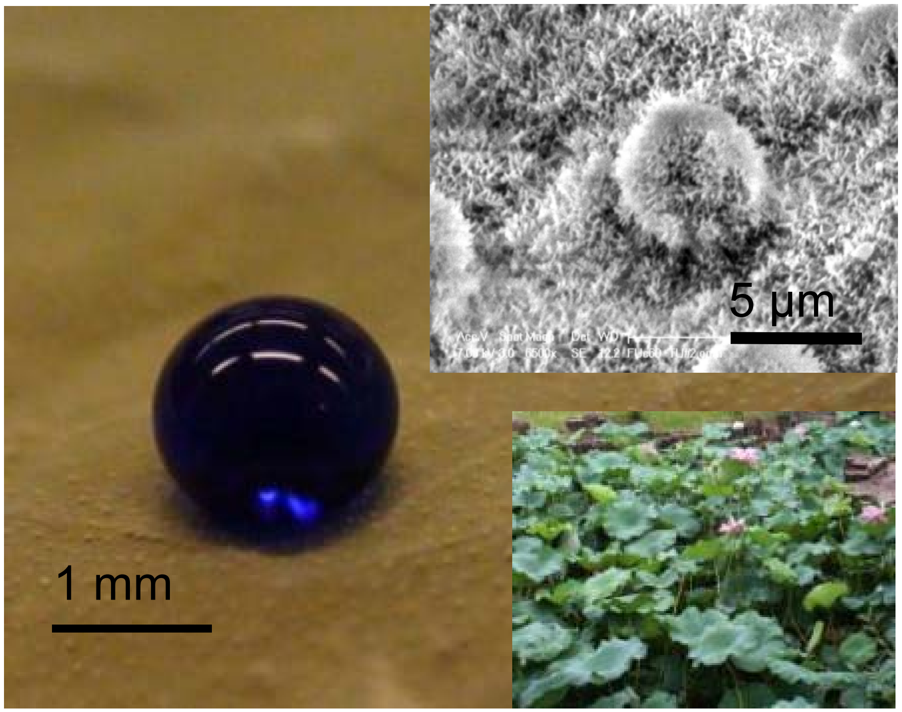
The Lotus Leaf

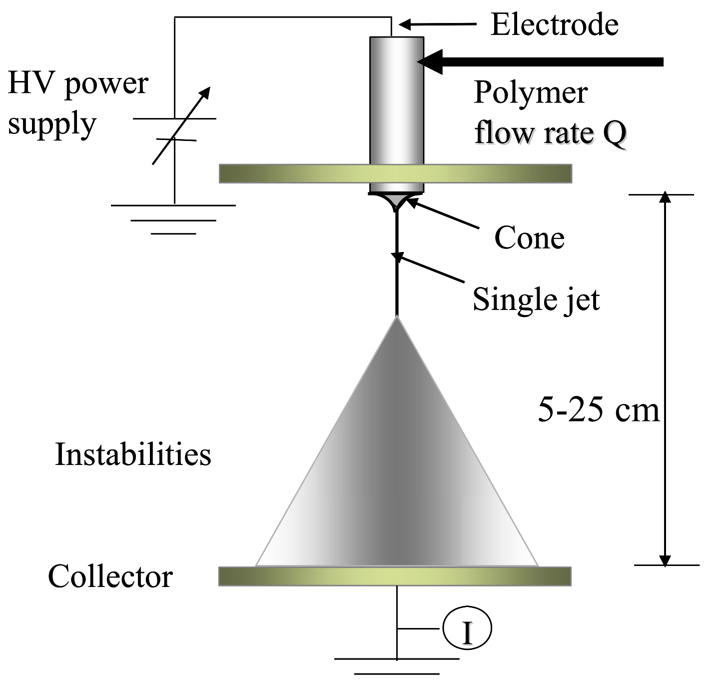


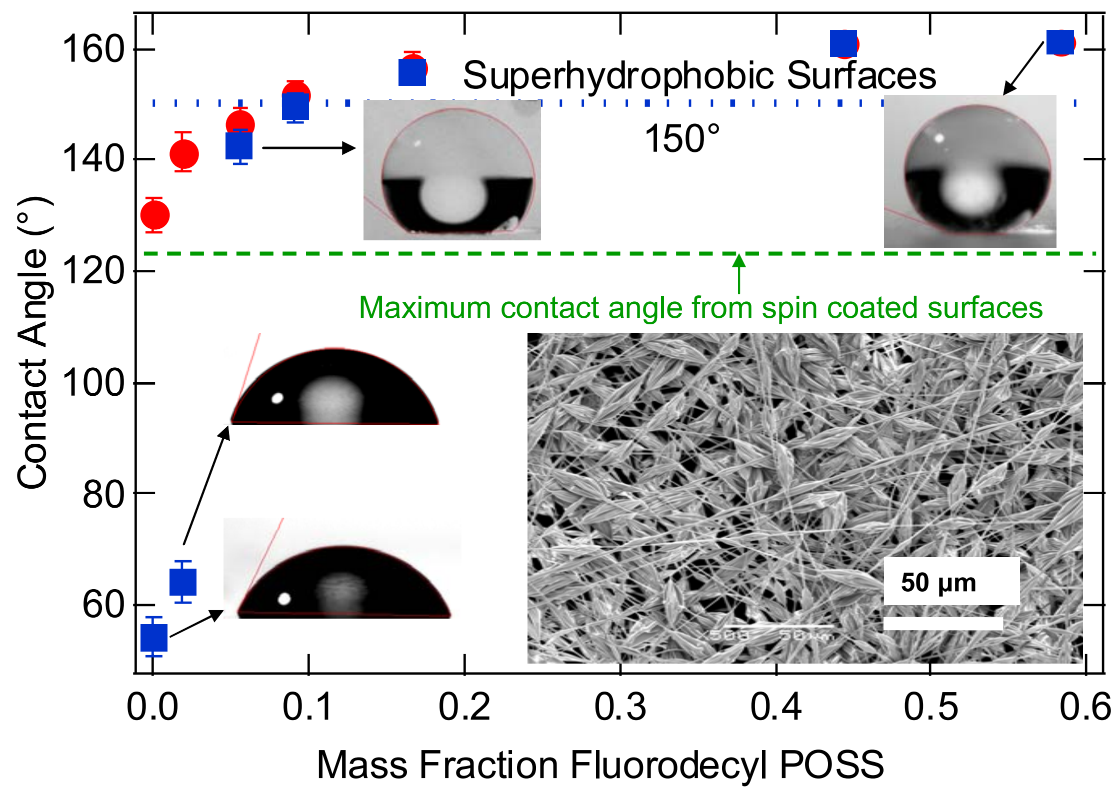
Water, γ_{LV} = 72.1 mN/m

Hexadecane, γ_{LV} = 27.5 mN/m

On most surfaces, $\theta_{oil} < \theta_{water}$. This is because the surface tension (γ_{lv}) of water is significantly higher than that for oils.

Electrospun Surfaces



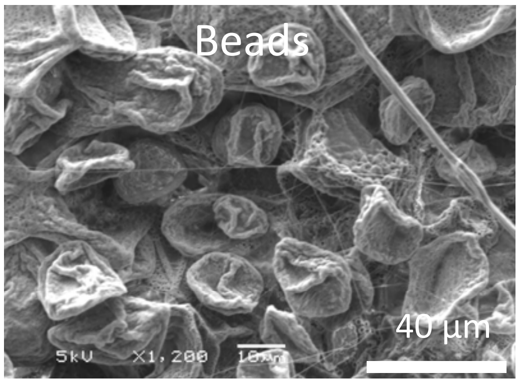


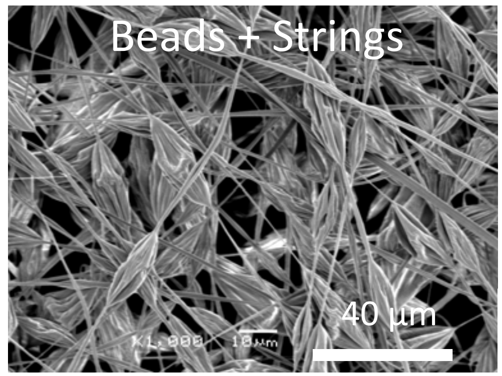
- ‘Beads on a string’ morphology, with high roughness and porosity
- A single step process - surface turns superhydrophobic for all POSS concentrations > 10 wt%

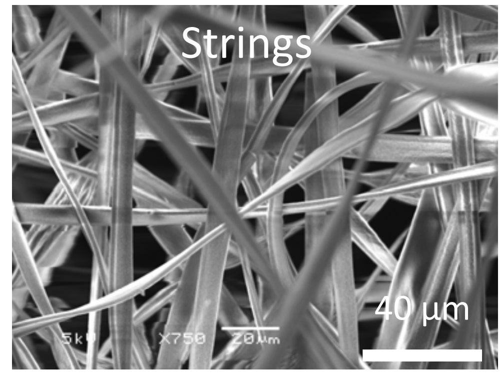
Science (2007)

Effect of Surface Texture

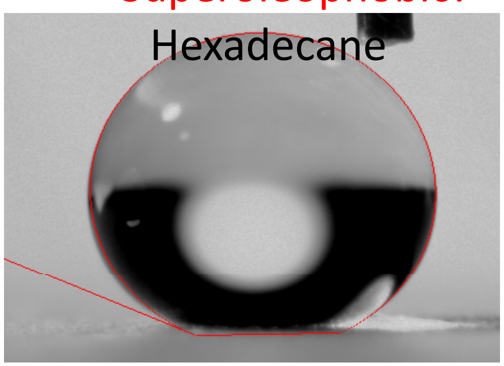
Each surface is composed of PMMA+POSS – 44 wt% blend; contact angle for hexadecane on corresponding spincoated surfaces = $q_{adv} = q_{rec} = 79°$.

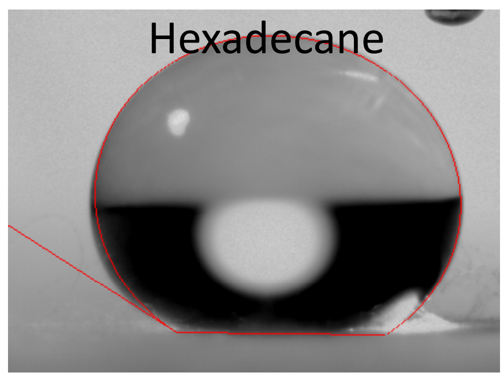


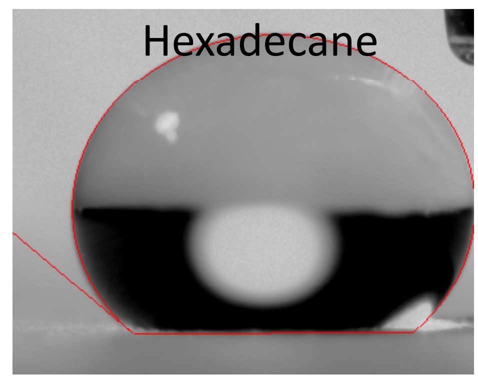




Superoleophobic!







$q^*_{adv} = 156°$ | $q^*_{adv} = 153°$ | $q^*_{adv} = 147°$

$q^*_{rec} = 150°$ | $q^*_{rec} = 141°$ | $q^*_{rec} = 120°$

Water contact angles

$q^*_{adv} = q^*_{rec} = 165°$ | $q^*_{adv} = q^*_{rec} = 163°$ | $q^*_{adv} = q^*_{rec} = 162°$

Science (2007), *PNAS* (2008).

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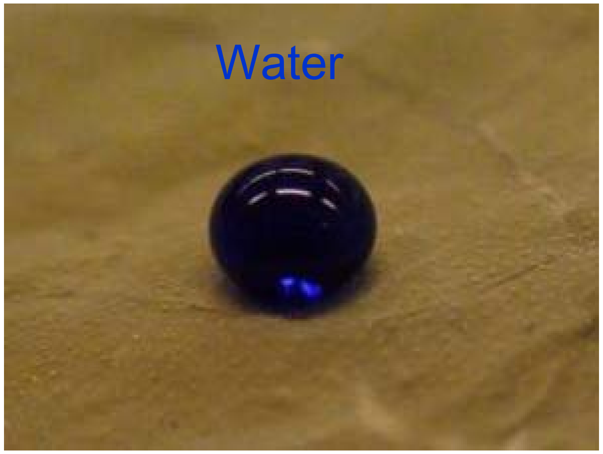
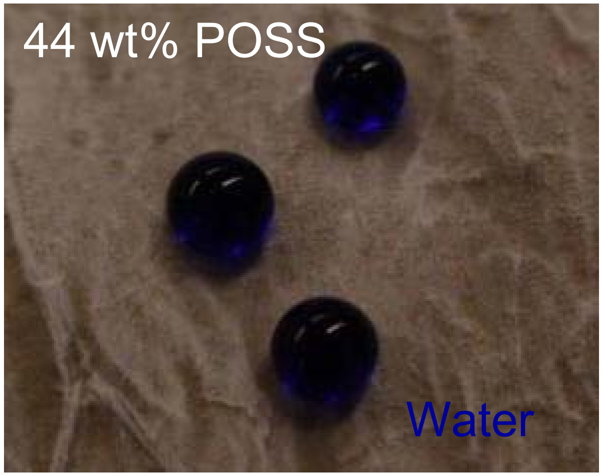
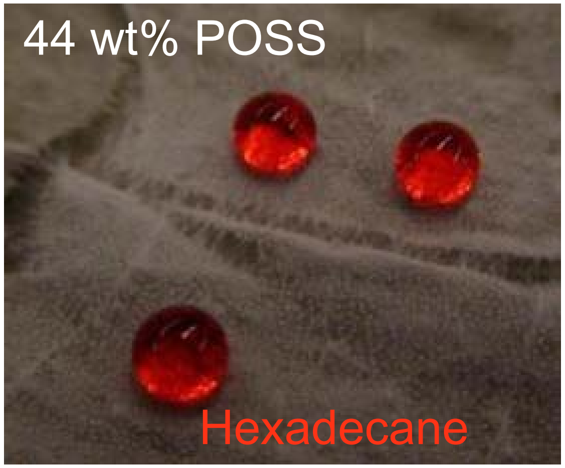
Comparison with Lotus Leaf



Coat with electrospun fibers

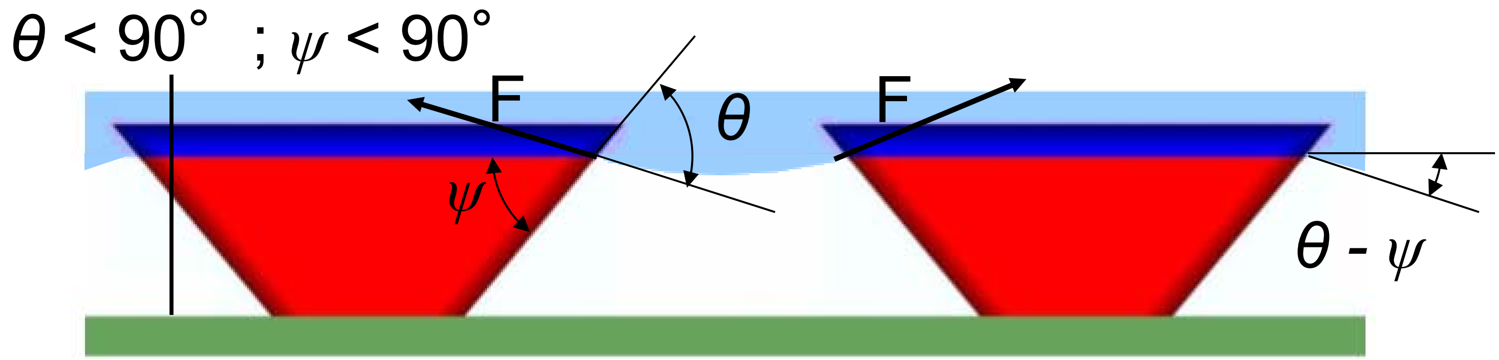


Coat with electrospun fibers



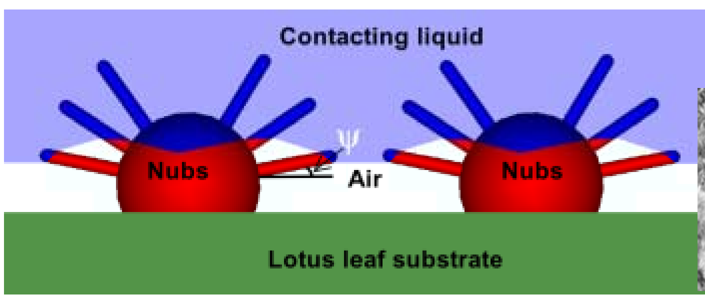
Science (2007), *PNAS* (2008).

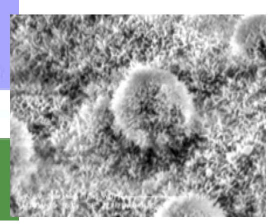
Critical role of re-entrant texture (ψ < 90°)



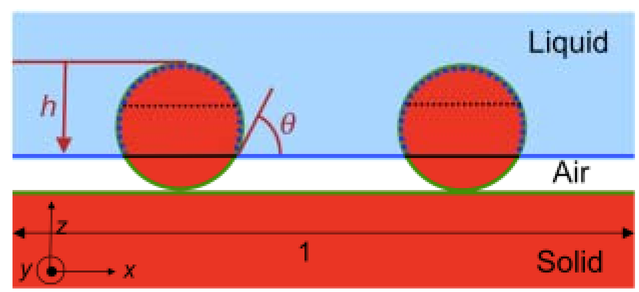
It is possible to support a composite interface even if θ < 90˚

Re-entrant curvature : 180˚ > θ > 0˚





Lotus Leaf



Cylinders / Fibers

Herminghaus, *Euro. Phys. Lett.* (2000), *Science* (2007); PNAS (2008)

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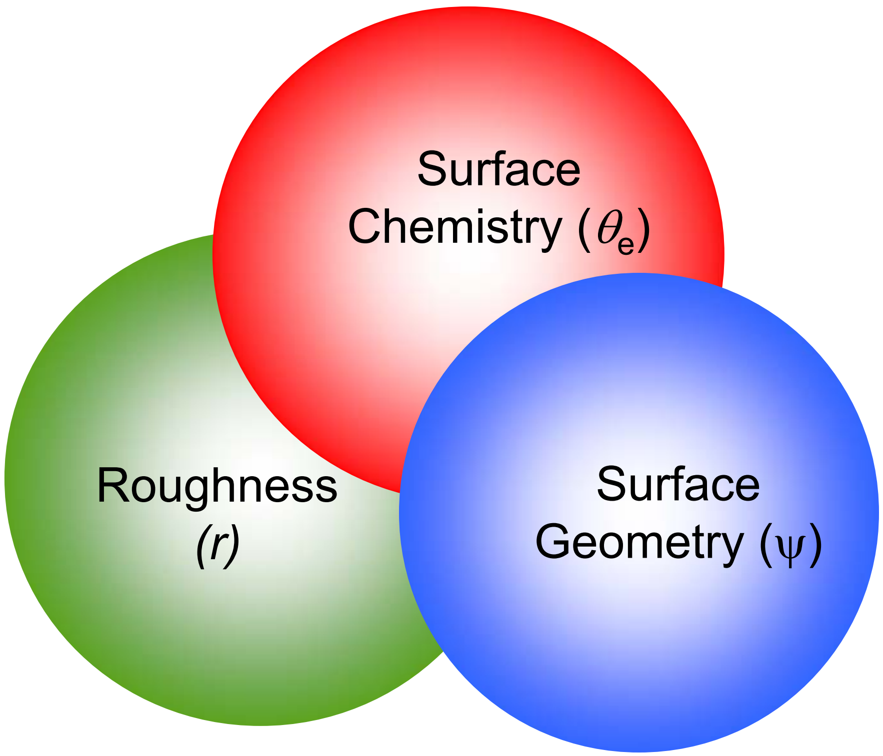
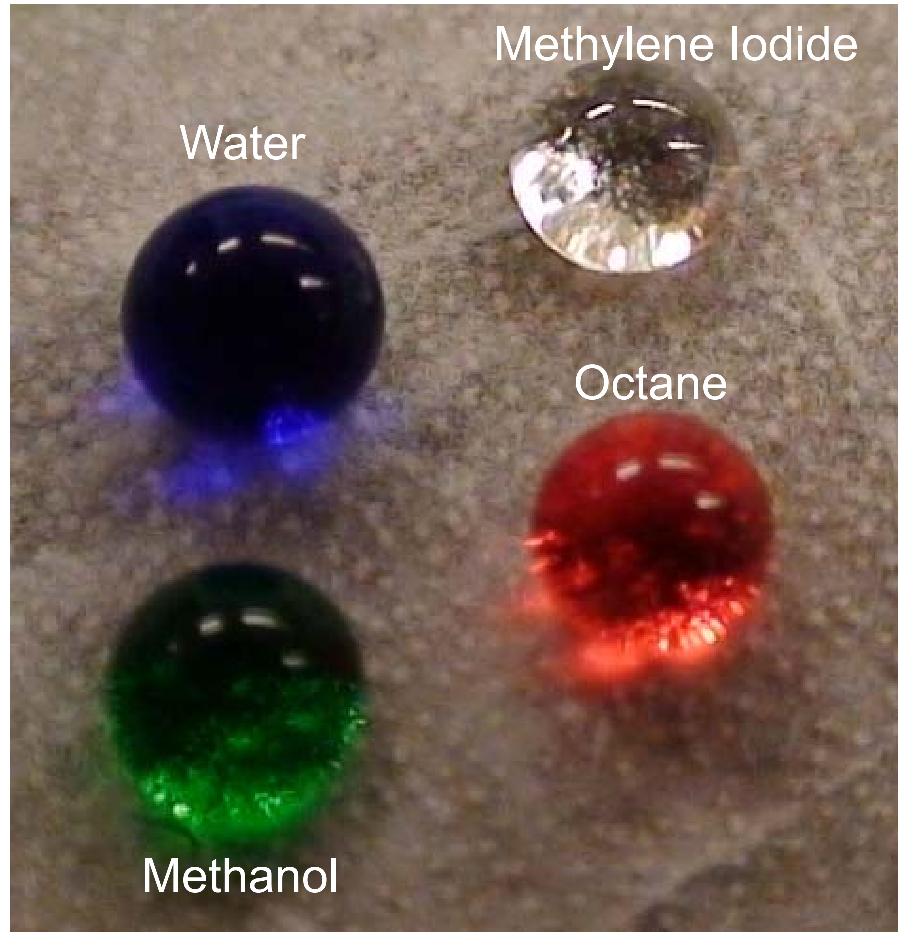
Designing Omniphobic Surfaces

- **Constructing super-repellent surfaces**
  - Three key ingredients



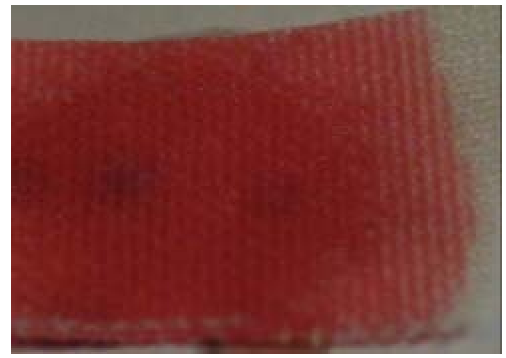


PMMA + 44 wt% POSS
electrospun coating (beads on a string) morphology

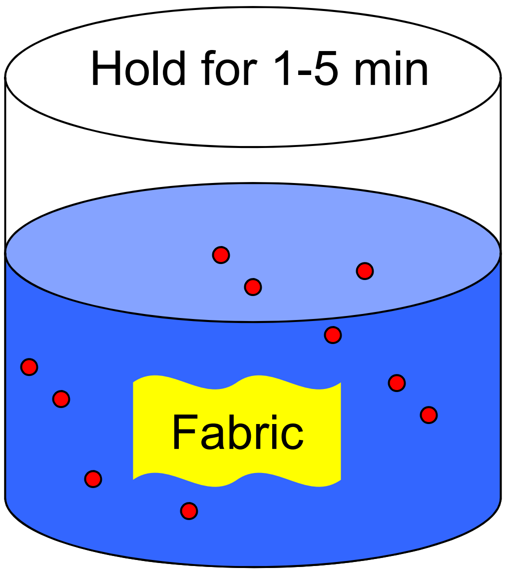
Science (2007)

The Dip-Coating Process

Hexadecane (γ_{lv} = 27.5 mN/m) on an as-received commercial polyester fabric



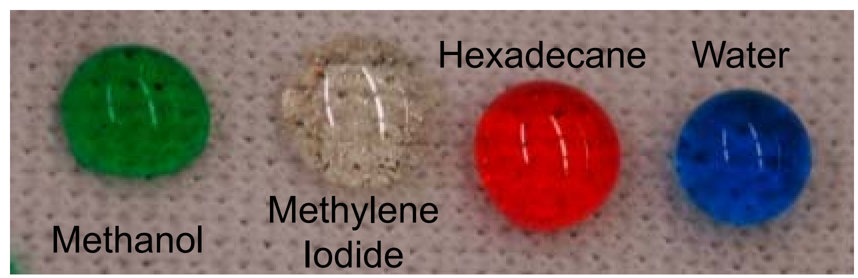
Before



Dip

Solution of fluorodecyl POSS in Asahiklin (30 mg/ml)

Dry (heat in oven at 60° C for 20 minutes)



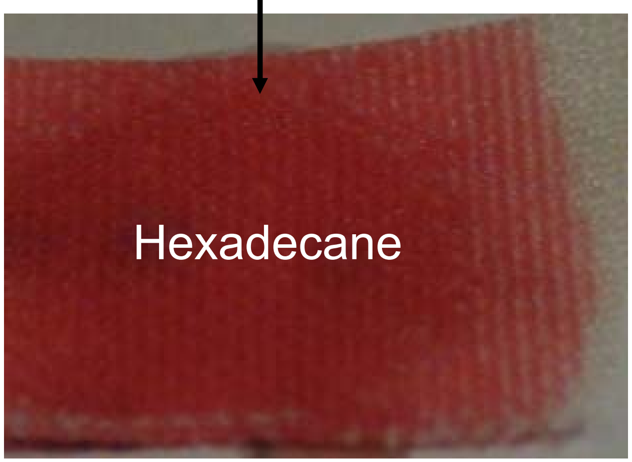
After dip-coating with a solution of fluorodecyl POSS

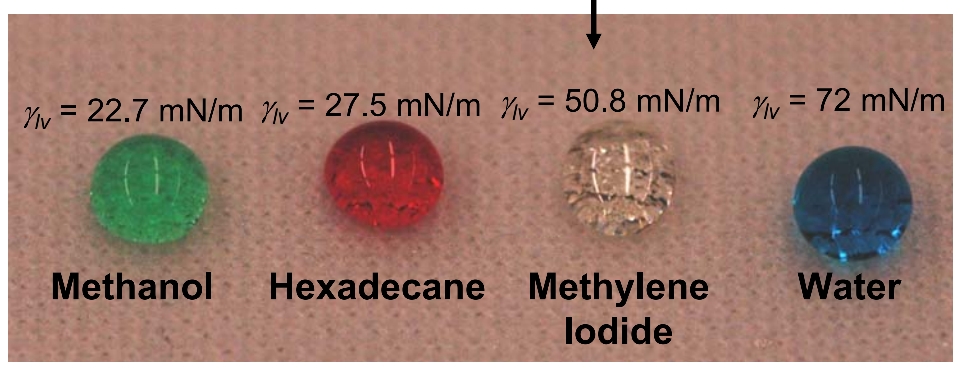
Adv Mater (2008)

Dip-Coated Polyester Fabric

Before coating

After coating with fluorodecyl POSS in Asahiklin (30 mg/ml)





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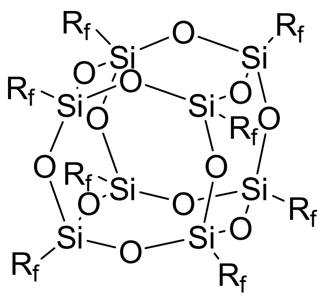
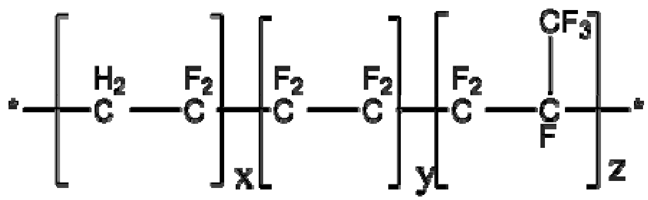
Dip-coating process for conformal coating of textured surfaces



R_f = $-CH_2-CH_2-(CF_2)_7-CF_3$
Fluorodecyl POSS
$\gamma_{sv} \approx 8$ mN/m



Tecnoflon® (BR9151)
Fluoro-elastomer from
Solvay-Solexis
$\gamma_{sv} \approx 18$ mN/m

50:50 mixture, total solids = 10 mg/ml

Dip in Asahiklin solution for 5 minutes

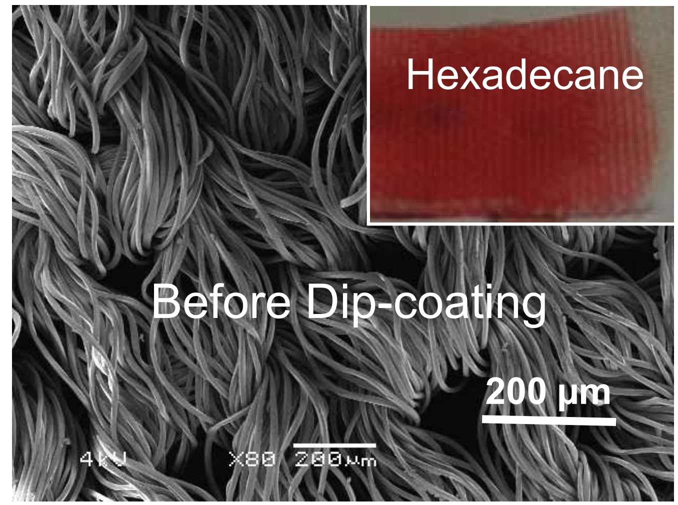
↓

Air dry to remove solvent

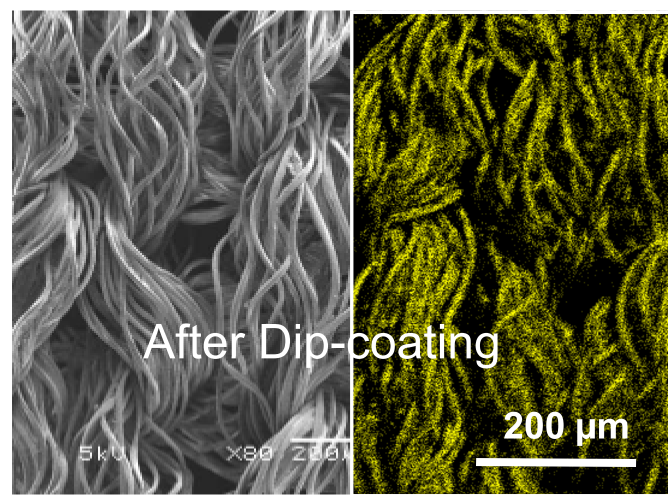
↓

Heat treat at 60 °C for 30 minutes

Anticon 100 polyester fabric



EDAXS spectrum for fluorine



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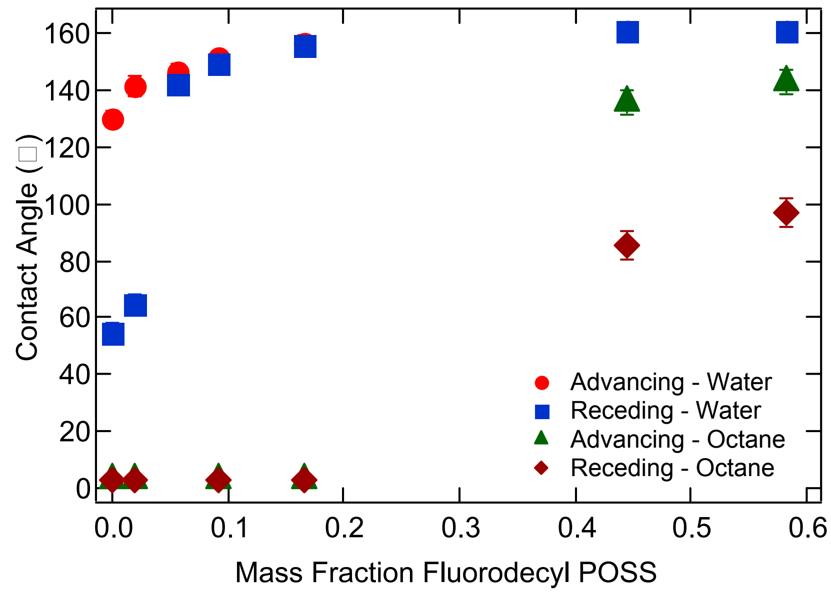
Superhydrophobic/Superoleophilic

Designing Superoleophobic Surfaces

Anish Tuteja,[1] Wonjae Choi,[2] Minglin Ma,[1] Joseph M. Mabry,[3] Sarah A. Mazzella,[3] Gregory C. Rutledge,[1] Gareth H. McKinley,[2*] Robert E. Cohen[1*]

Superhydrophobic Superoleophilic

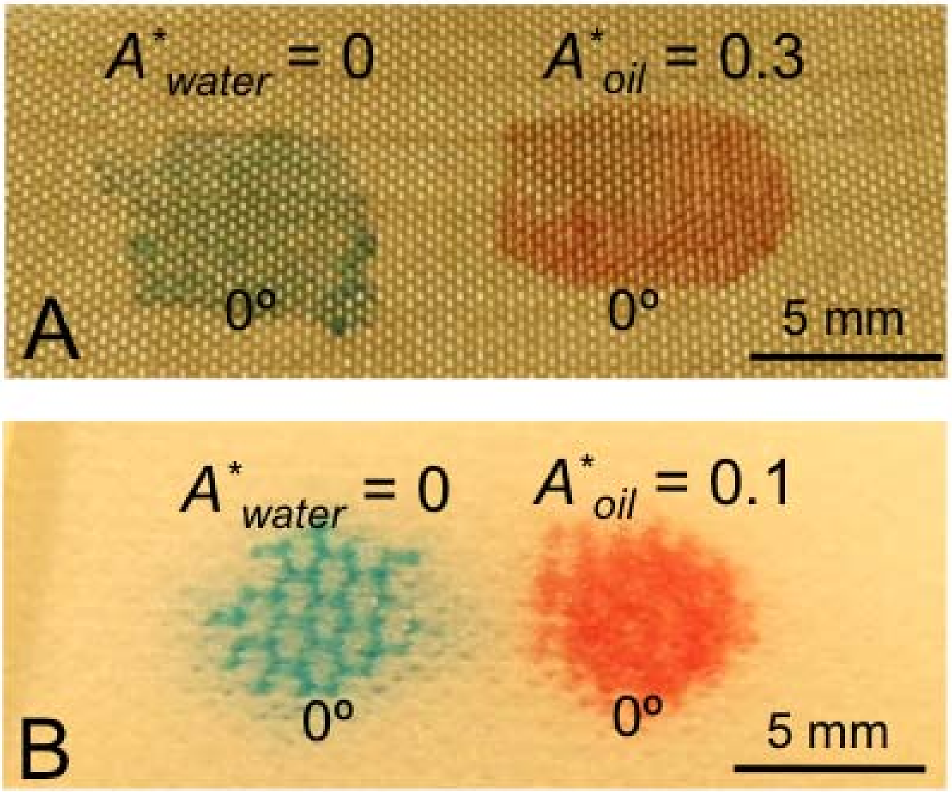


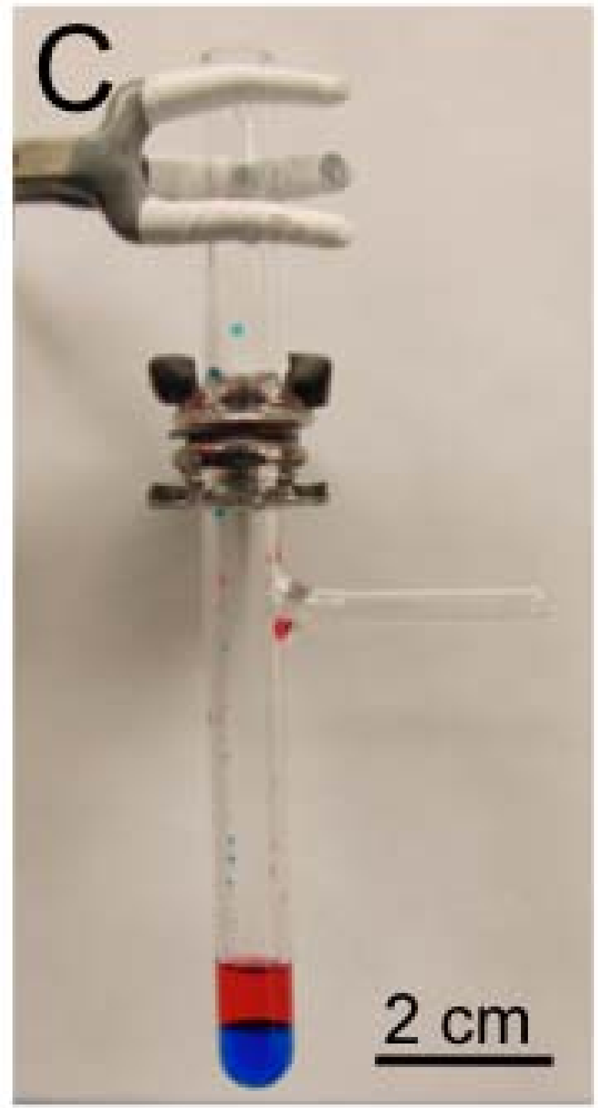
At low POSS concentrations many surfaces are *both* superhydrophobic and superoleophilic ($\theta^*_{alkane} \approx 0°$). Thus, these porous surfaces form ideal membranes for separating mixtures / dispersions of alkanes (oils) and water

But…water is more dense than hydrocarbons!

Science (2007)

Hydrophilic Membranes





A and **B.** Neat x-PEGDA dip-coated stainless steel mesh 100 and polyester fabric **C.** An apparatus with a mesh 100 coated with neat x-PEGDA Both water and rapeseed oil permeate through.

Manuscript in preparation

PEGDA + Fluorodecyl POSS

Can hydrogen bond with water

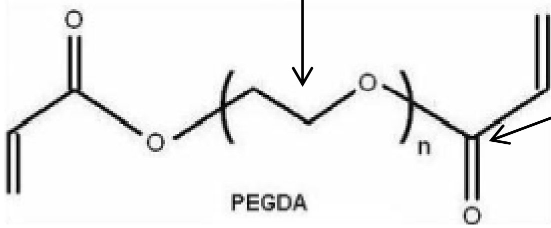
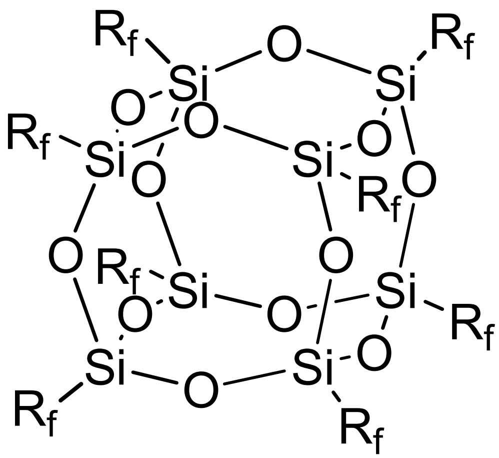


Photo-crosslinkable



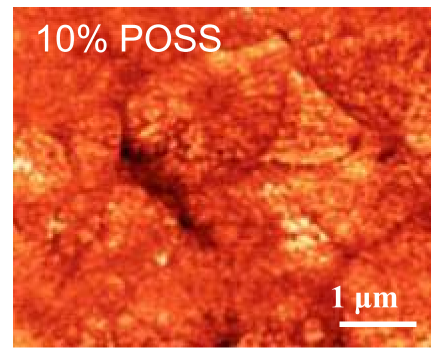
$R_f = -CH_2-CH_2-(CF_2)_7-CF_3$

Fluorodecyl POSS

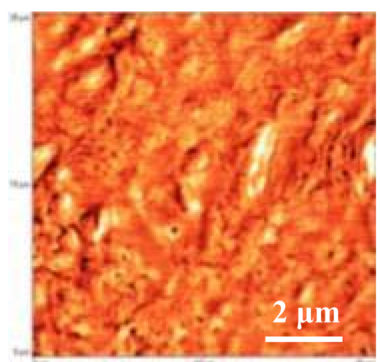
$\gamma_{sv} \approx 8$ mN/m

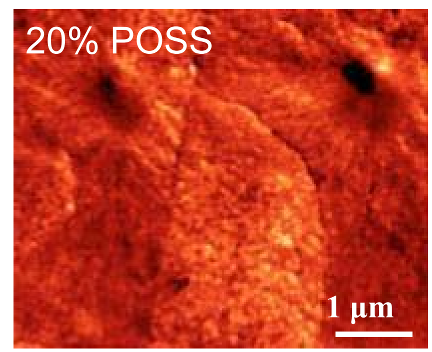
Fluorodecyl POSS molecules preferentially segregate to the air interface and crystallize.

AFM Phase images of spin-coated PEGDA + POSS films



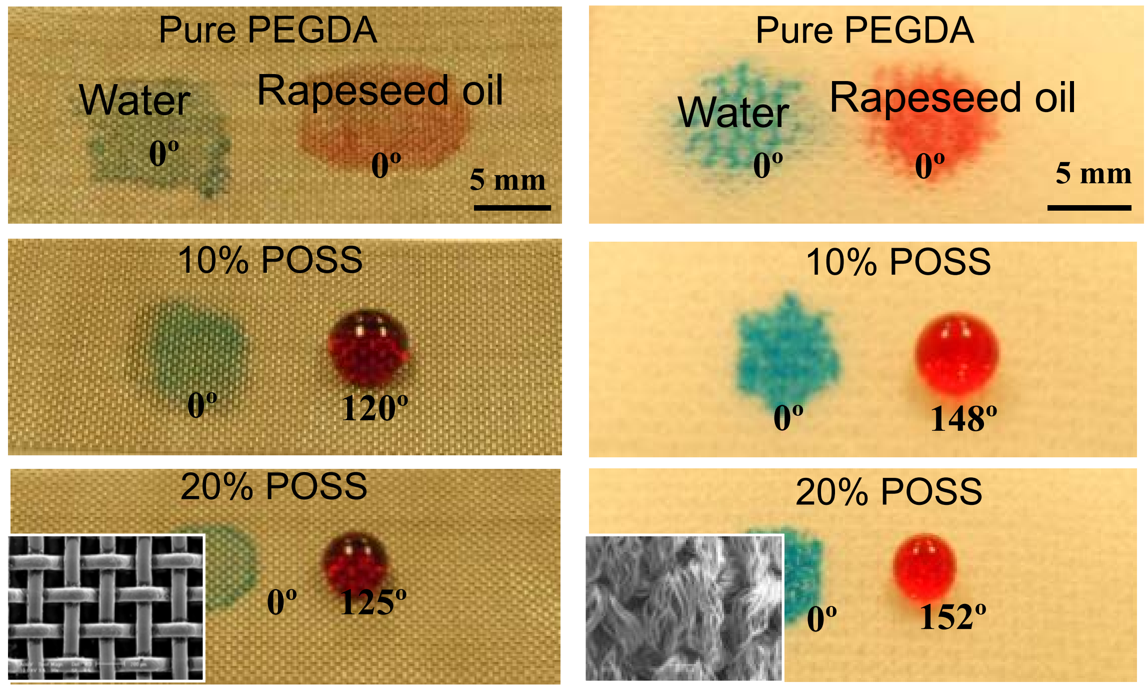
20% POSS
Under water





PEGDA + Fluorodecyl POSS Blends

Surfaces with inherent re-entrant curvature **dip-coated** with PEGDA + POSS blends



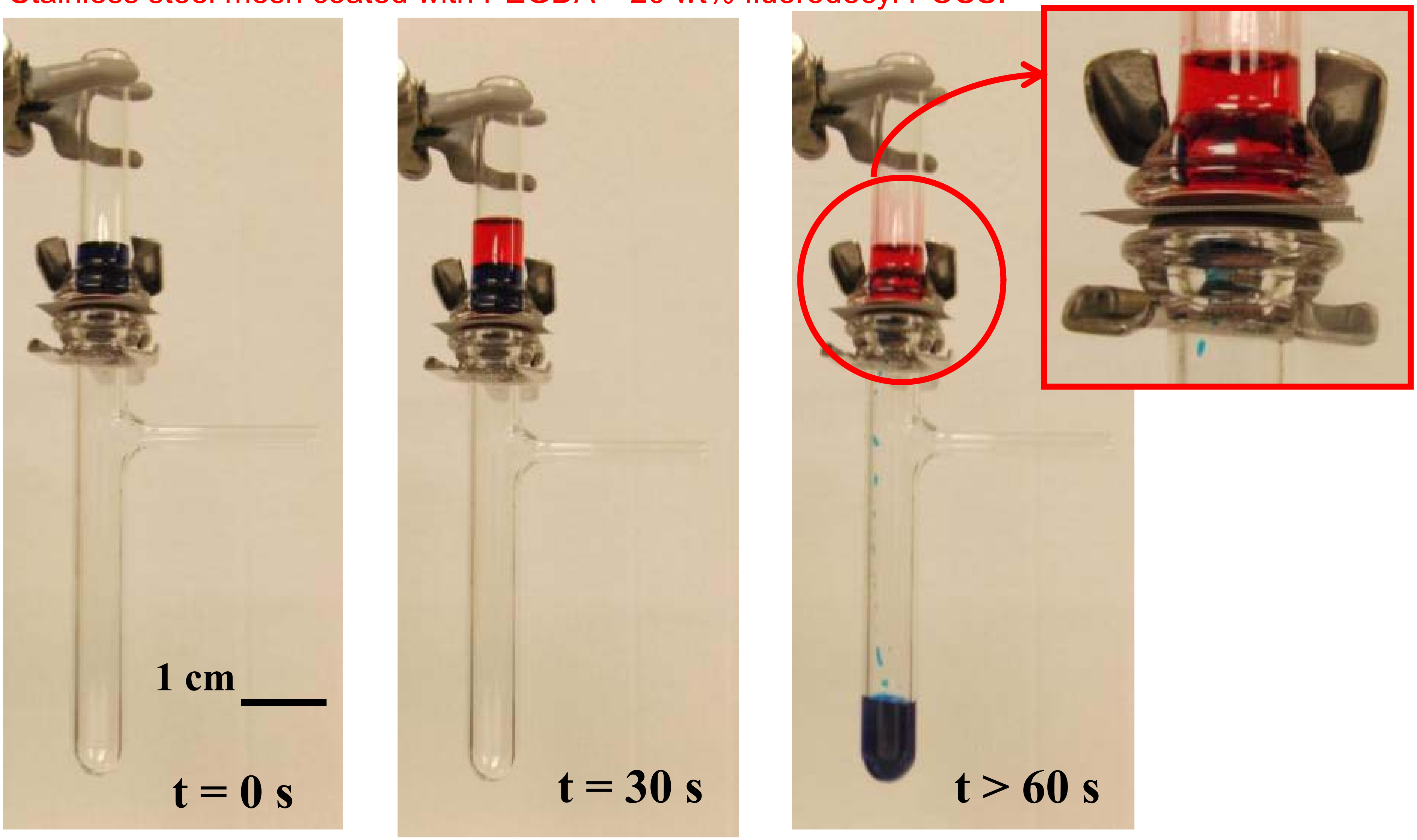
Stainless Steel Wire Mesh   Commercial Polyester Fabric

PEGDA surface reconfiguration leads to superhydrophilic behavior.

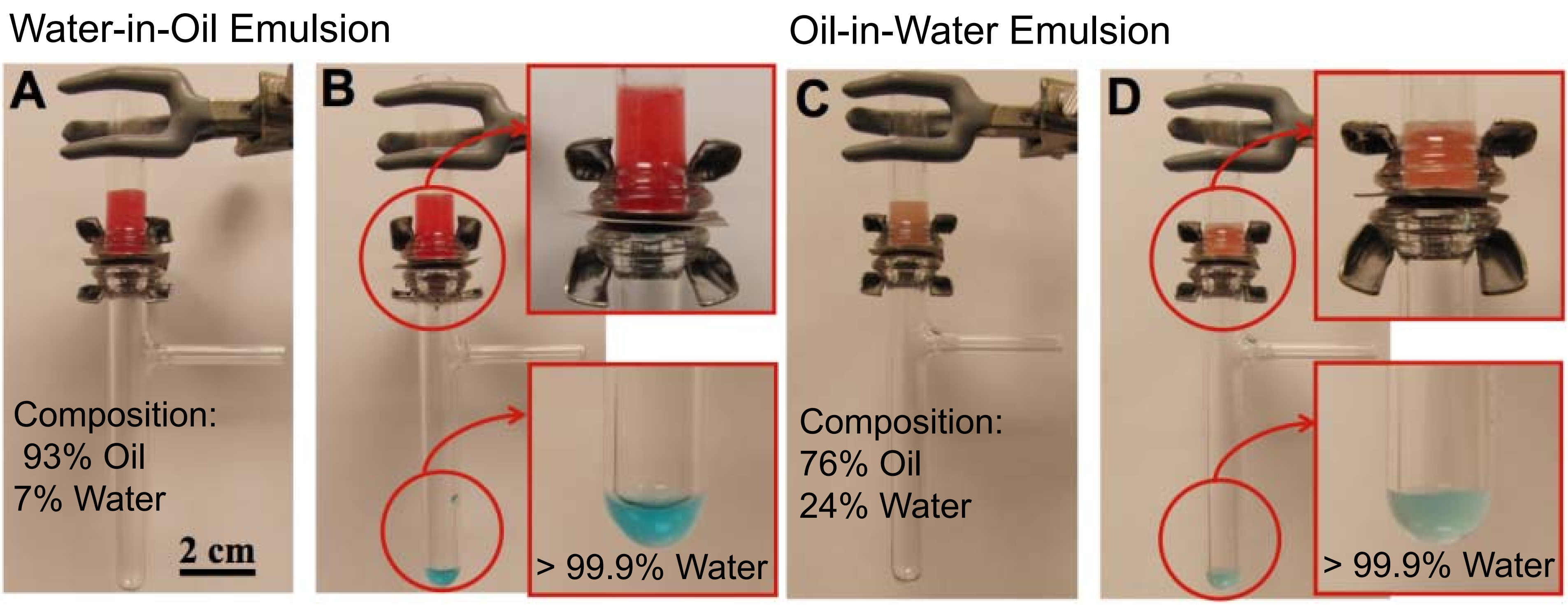
Manuscript in preparation

Free Oil – Water separation

Stainless steel mesh coated with PEGDA + 20 wt% fluorodecyl POSS.



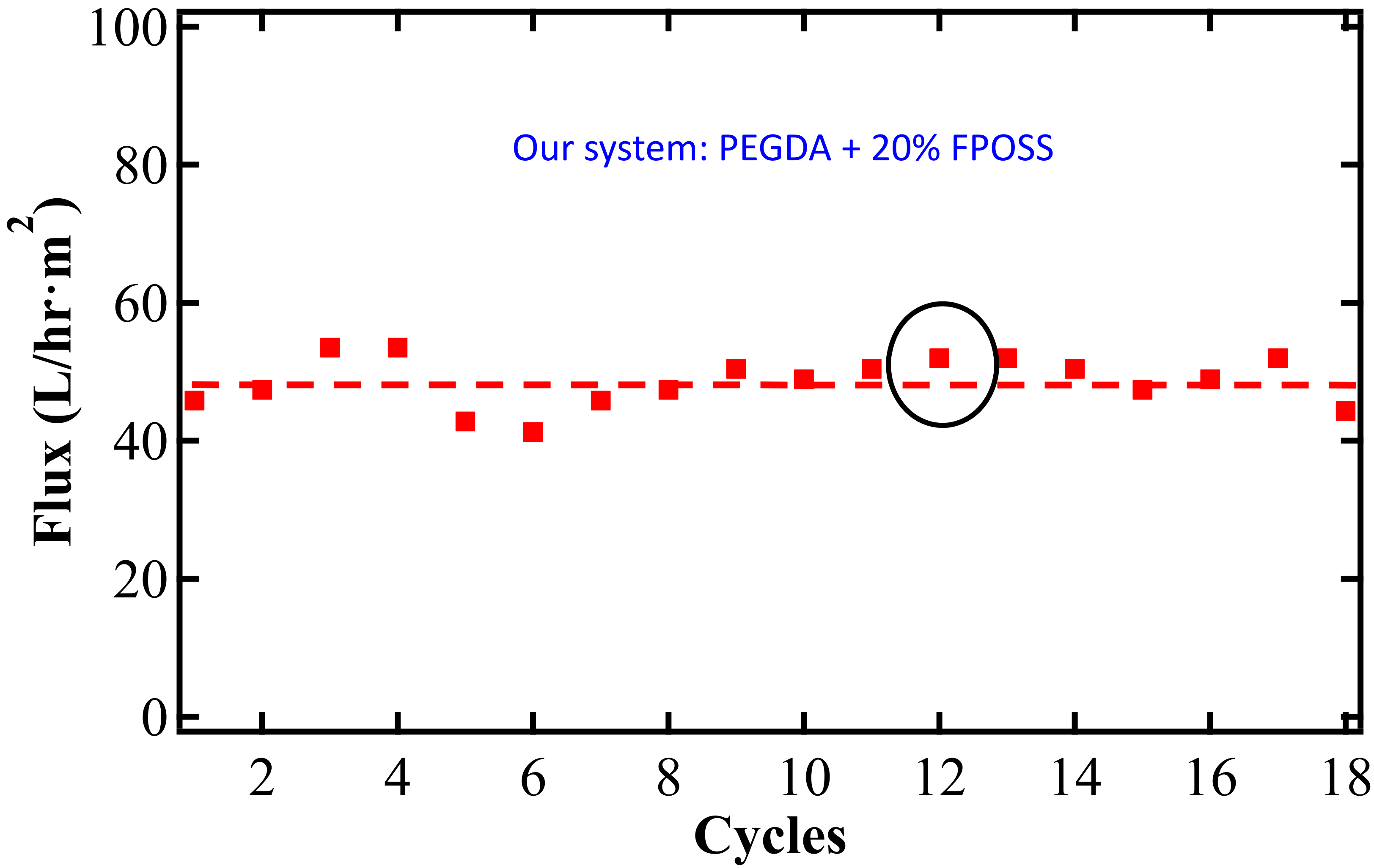
Separation of Oil-Water Emulsions



A simple, scalable, gravity-based system for the separation of both oil-in-water and water-in-oil emulsions. This is one of the first gravity-based systems to achieve such high emulsion separation efficiencies.

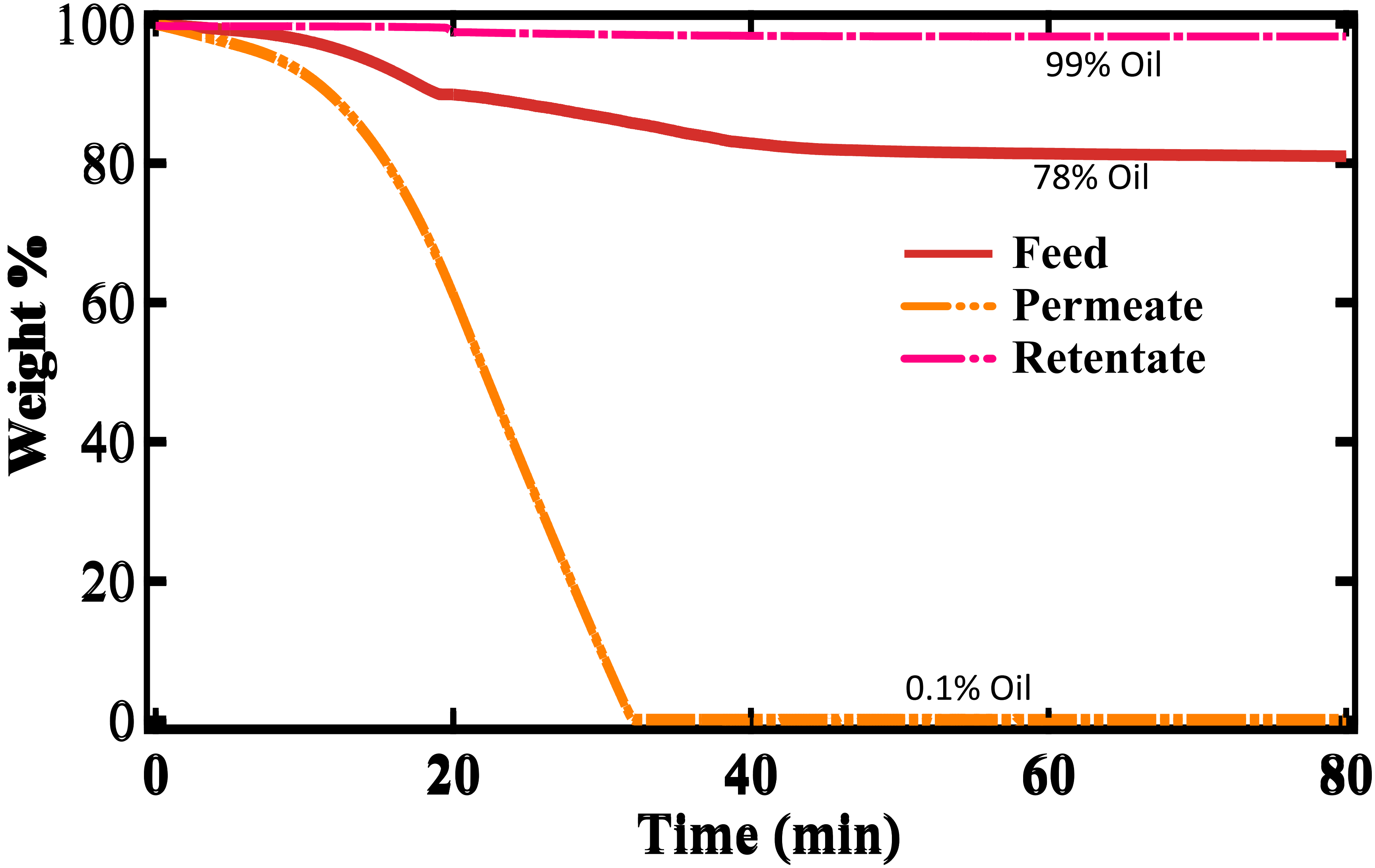
Manuscript in preparation

Oil-Water Emulsion Separation



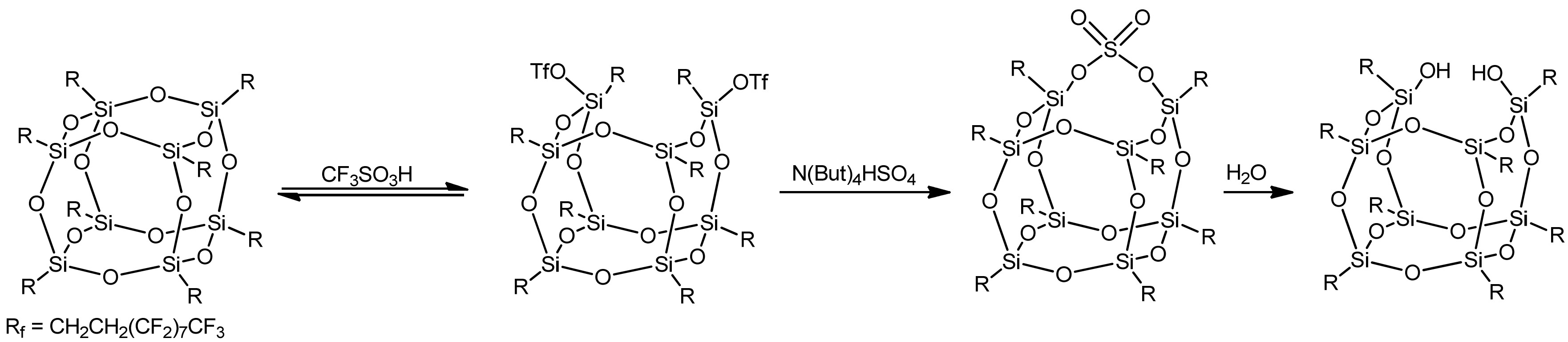
Manuscript in preparation

Separation Efficiency



Manuscript in preparation

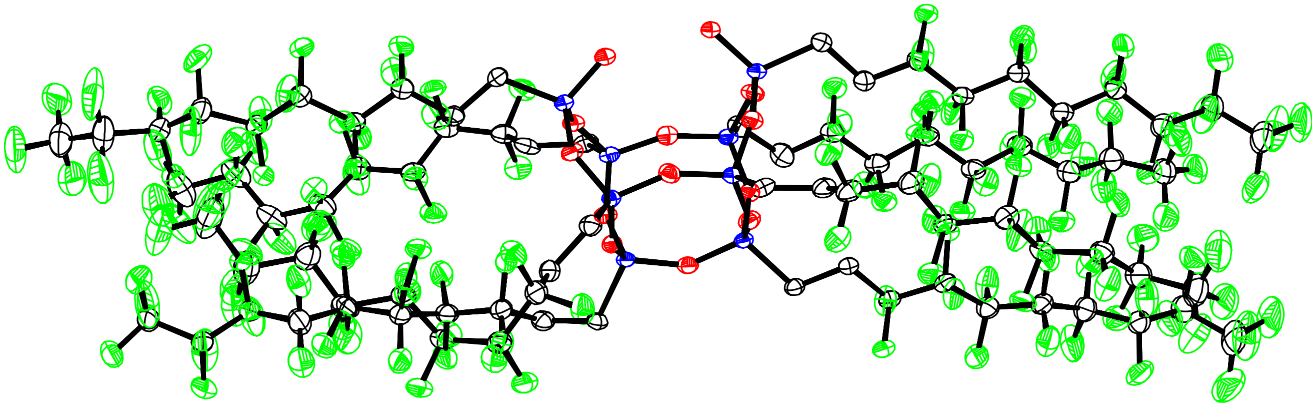
Incompletely Condensed Silsesquioxane



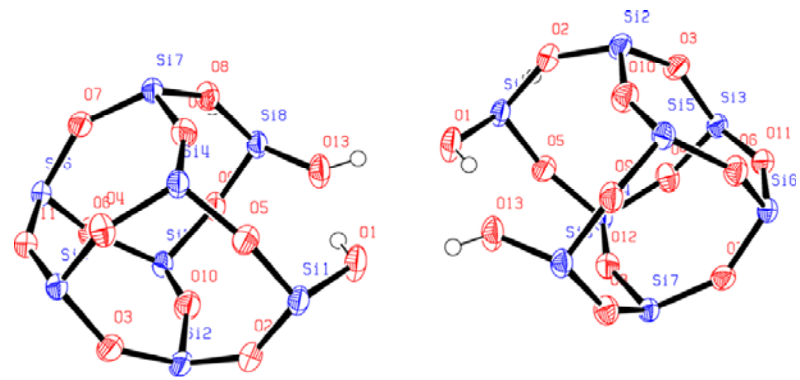
- Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.*

Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.,* **2011**, *133*, 20084.

X-Ray Crystal Structure of Disilanol

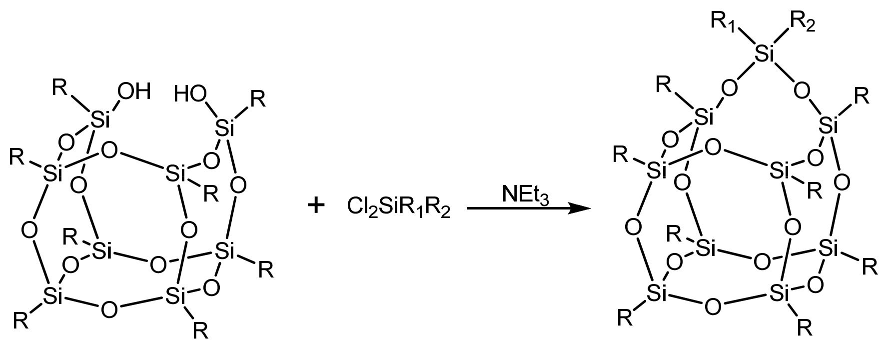


- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- M_r=,monoclinic, space group P2(1)/c , a=11.84(10) Å, b=57.11(6) Å, c=19.06(2) Å, α= 90.00°, β=92.21(10) °, γ=90.00 °, V= 12878(2) Å^3



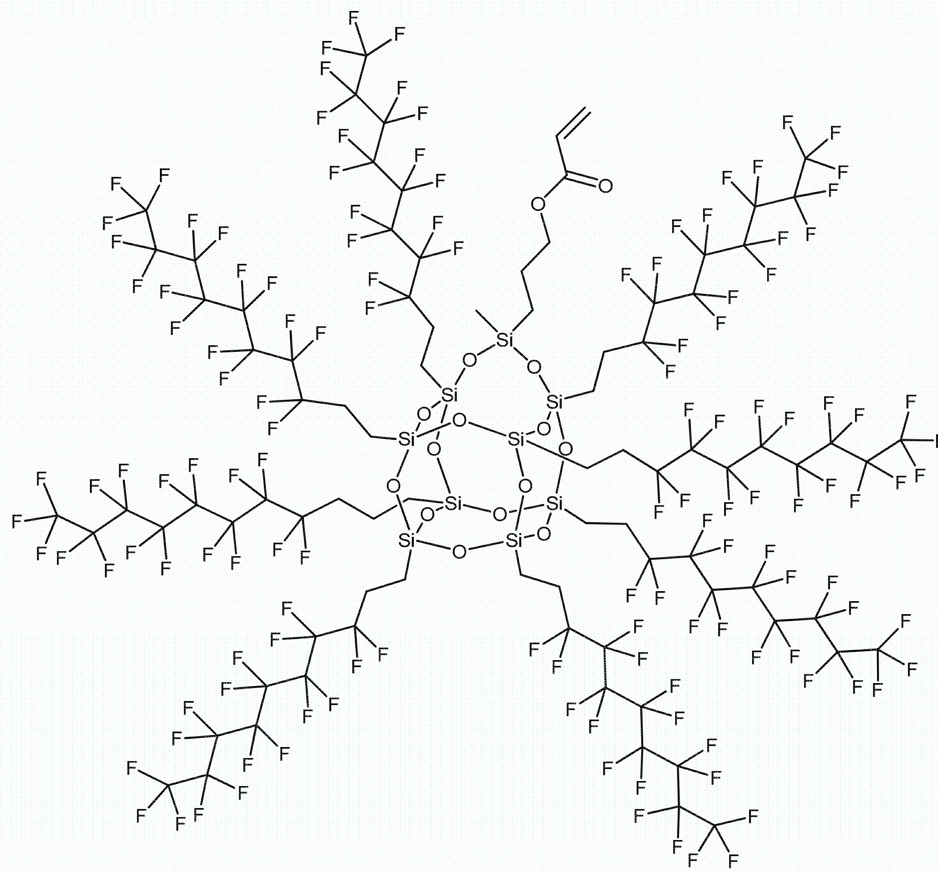
Ramirez, S. M.; Diaz, Y. J.; Campos, R. ; Stone, R.T.; Haddad, T.S.; Mabry, J.M., *J. Am. Chem. Soc.,* **2011**, *133*, 20084.

Edge Capping Reactions



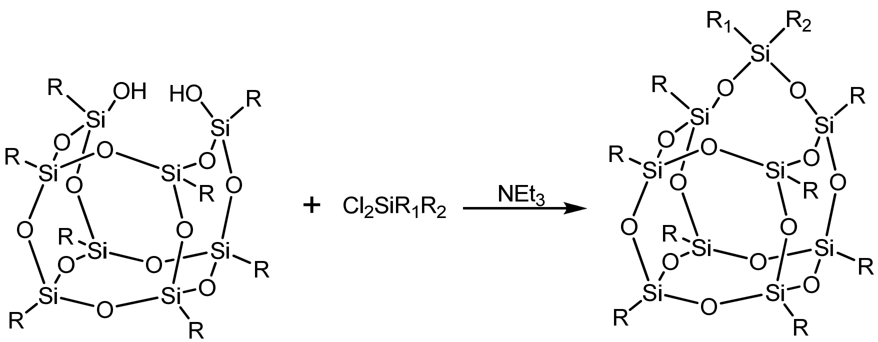
R = $CH_2CH_2(CF_2)_7CF_3$
R_1 = CH_3
R_2 = $CH_2CH_2CH_2$ OC(O)CHCH$_2$

- Edge capping reactions typically have 40-70% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes



Macromer/RBM = 4178 g/mol

Edge Capping Reactions



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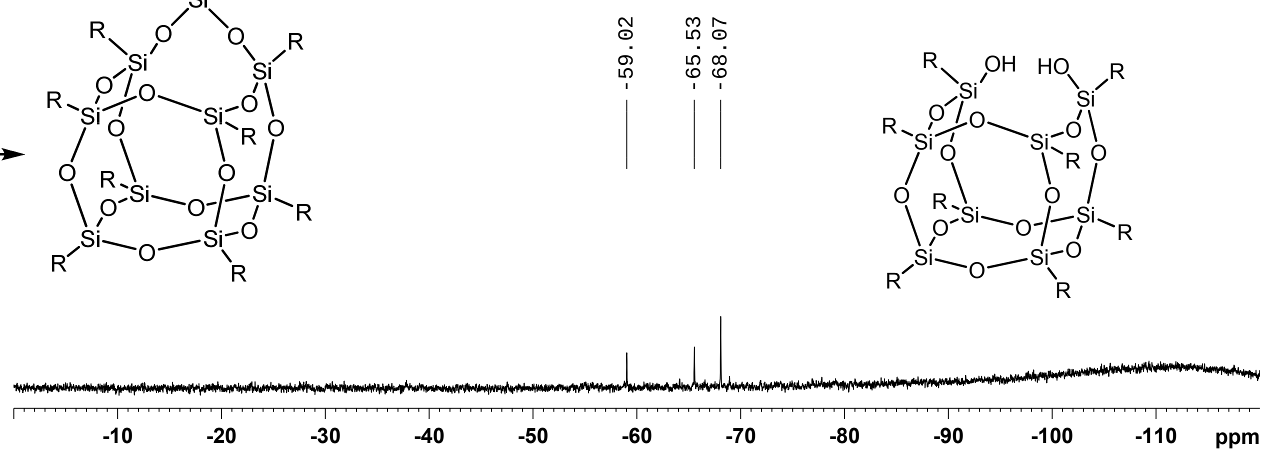
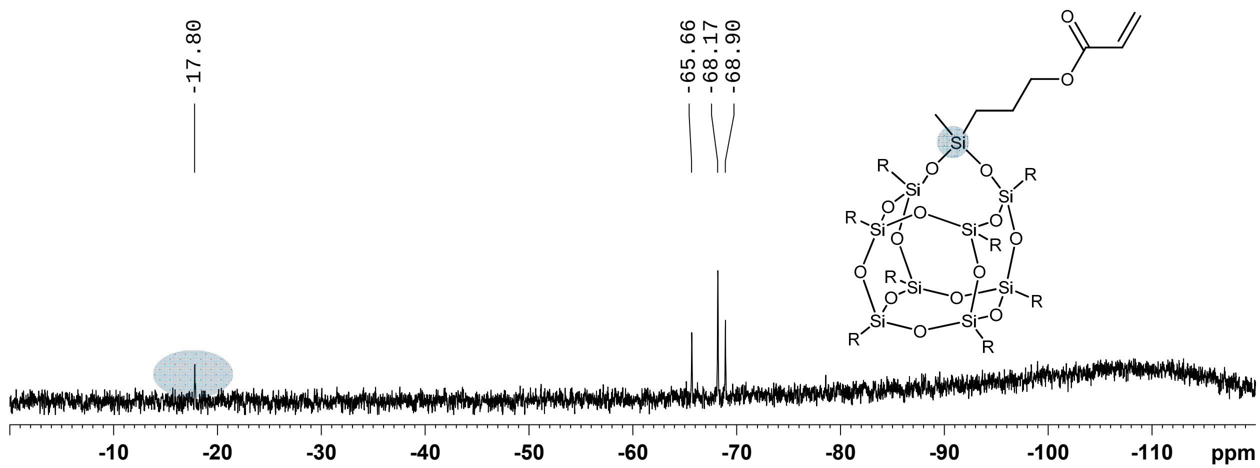
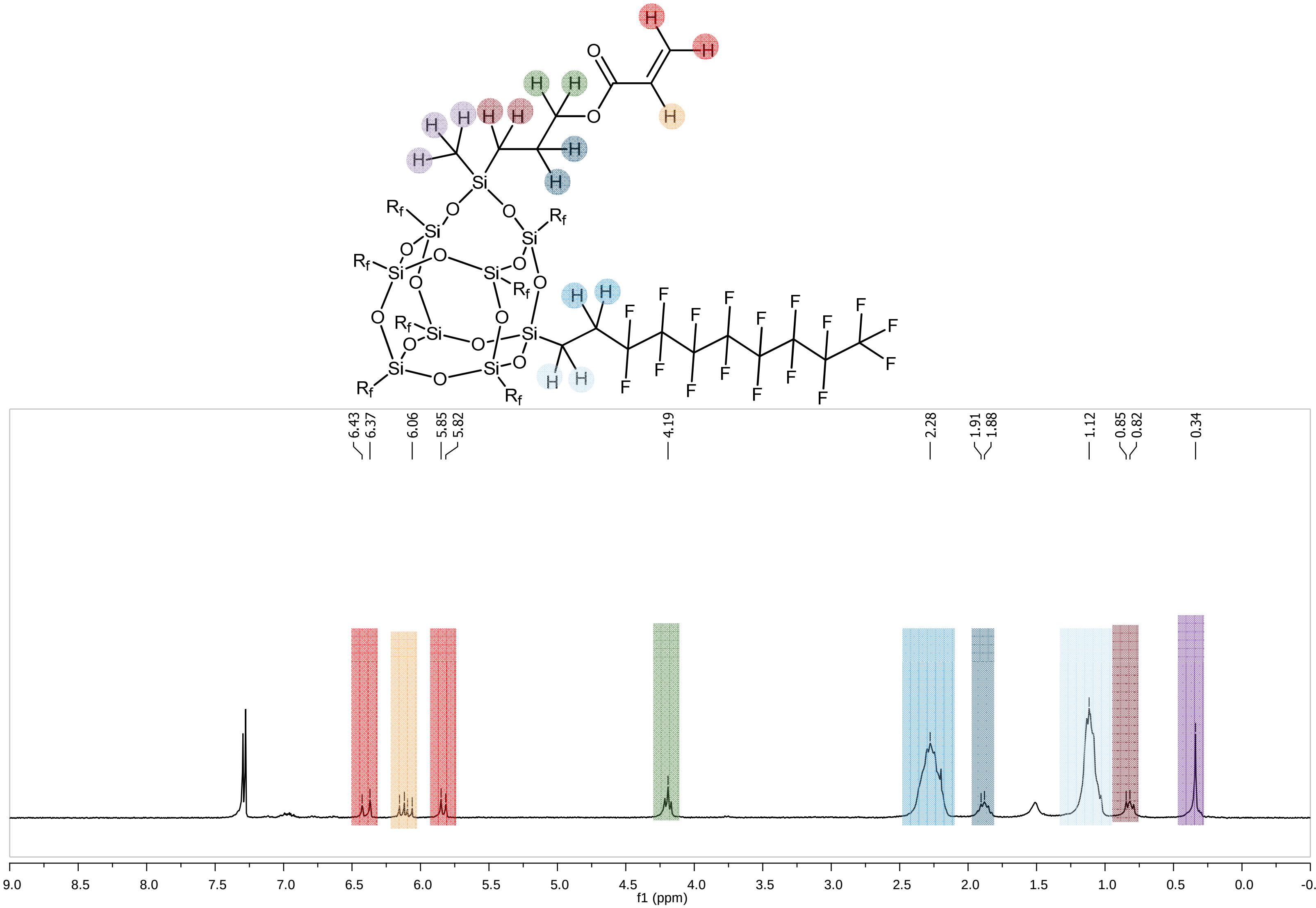




^{29}Si NMR taken in fluorinated solvent

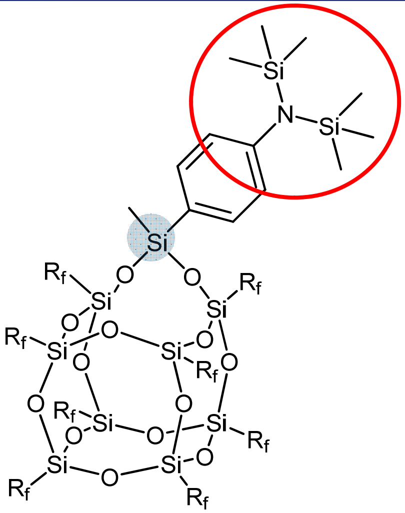
- Typically 40-70% yield
- Main side product is starting material (recycled), formed during base addition
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes
- Si ratio (1:2:2:4)
- **New Si peak!**

1H NMR Characterization of Compounds

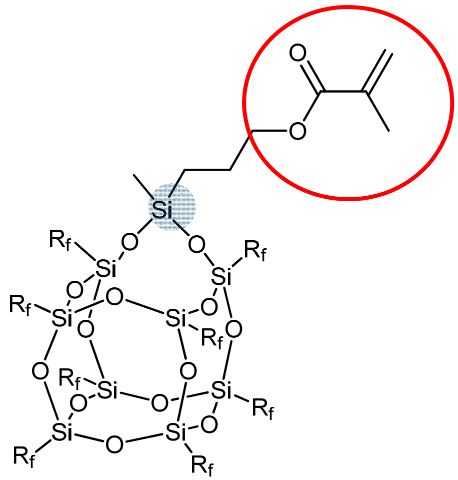


^{19}F NMR taken in diethyl ether. ^{1}H NMR taken in $C_6F_6/CDCl_3$ mixture.

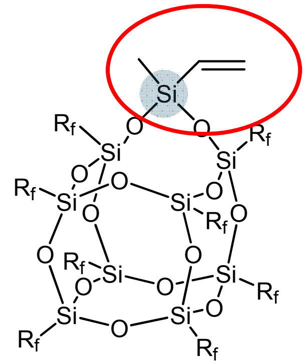
F-POSS Structures Synthesized



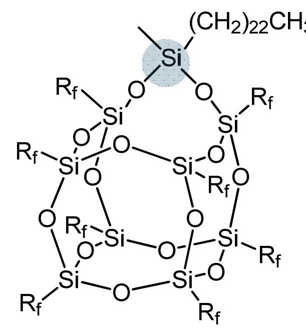
-29.5 ppm



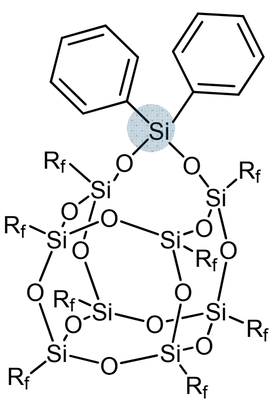
-17.8ppm



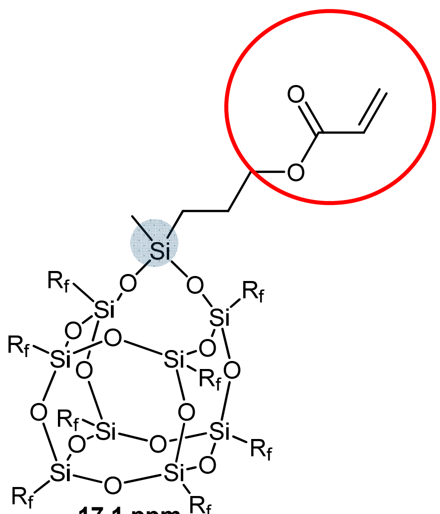
-32.1 ppm



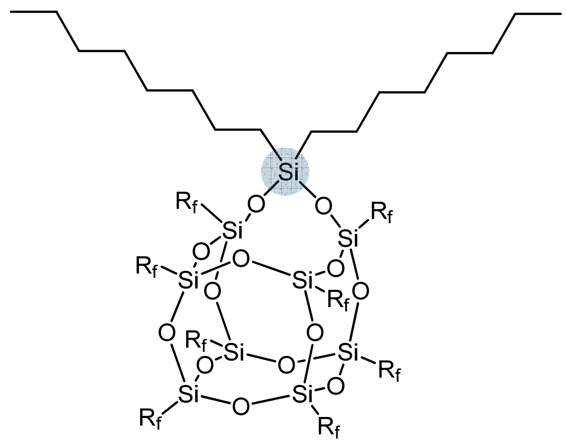
-17.8 ppm



-45.5 ppm



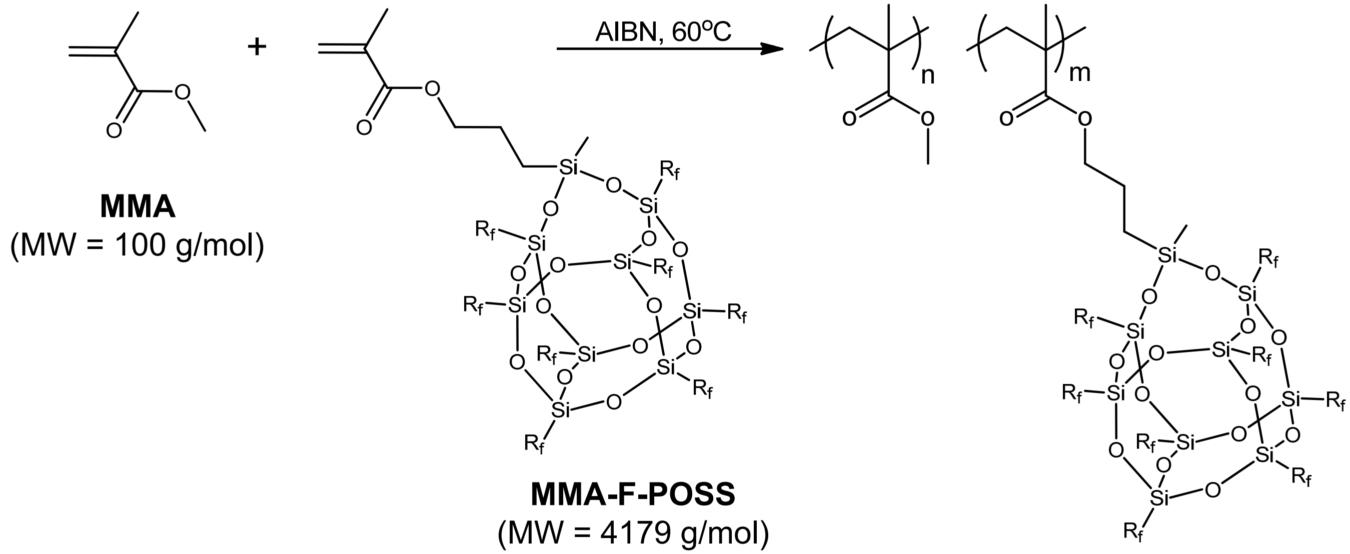
-17.1 ppm



-17.9 ppm

R = $CH_2CH_2(CF_2)_7CF_3$

Initial Copolymerizations



Sample #	Weight (g) MMA-F-POSS	MMA	Weight (%)F-POSS	Monomer (mmol) MMA-F-POSS	MMA	Mol Ratio (MMA:MMA-F-POSS)	Initiator (mol %)	Conversion (%)	Weight (%) FPOSS*
1	0.085	1.31	6.3	0.02	13.1	655	0.5	42	2.74
2	0.362	1.31	21.6	0.09	13.1	145	0.2	71	14.4
3	0.50	3.50	12.5	0.12	35.0	291	1		
4	1.00	3.00	25.0	0.24	30.0	125	1	62.5	
5	2.00	2.00	50.0	0.47	20.0	42	0.2	92.5	

*Weight (%) of F-POSS was calculated from elemental analysis of Fluorine content in the final polymer.

Summary

- FluoroPOSS are superhydrophobic
- FluoroPOSS polymer composite surfaces can be superhydrophobic and superoleophobic
- Superhydrophilic and superoleophobic surfaces have been developed
- Such surfaces are ideal for the separation of both free-oil and oil-water emulsions
- These membranes, for the first time, allow continuous-flow oil-water emulsion separation
- Functionality will allow the covalent attachment of these low energy materials to substrates of choice

Acknowledgements

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Superoleophobic Surfaces

Professor Anish Tuteja

Oil/Water Separation Membranes

Polymer Working Group

Fluorinated POSS

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Air Force Research Laboratory, Propulsion Directorate

Polymer Working Group

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Dr. Andy Guenthner
Mr. Brian Moore
Dr. Joe Mabry
Mr. Kevin Lamison
Dr. Josiah Reams

Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate

PWG Presentations

Who	What	When
Joe Mabry	Si Polymers & Composites	8:30
Andy Guenthner	Silicon Cyanate Esters	9:20
Sean Ramirez	F-POSS Disilanol	10:30
Anish Tuteja	Oil/water separation	10:55
Greg Yandek	Architecture effects on POSS	1:30

PWG Posters

Who	What
Andy Guenthner	Solubility Parameters
Tim Haddad	POSS Dianilines
Brian Moore	Architecture effects on solubility properties
Dana Pinson	Si-containing imide oligomers
Patrick Ruth	Silica-Reinforced Fluoropolymers
Kevin Lamison	Separation Membrane Breakthrough Pressure
Vandana Vij	Fluorinated silane modified perfluorooctynes
Yvonne Diaz	Incompletely-Condensed Fluorinated POSS


QUESTIONS?
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